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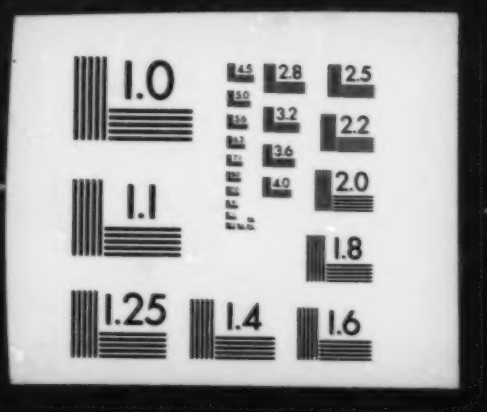

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Organophosphate and Organophosphorothionate Esters: Application of Linear Free Energy Relationships to Estimate Hydrolysis Rate Constants for Use in Environmental Fate Assessment

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ORGANOPHOSPHATE AND ORGANOPHOSPHOROTHIONATE ESTERS: APPLICATION OF LINEAR FREE ENERGY RELATIONSHIPS TO ESTIMATE HYDROLYSIS RATE CONSTANTS FOR USE IN ENVIRONMENTAL FATE ASSESSMENT

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ABSTRACT -- Hydrolysis rate constants required for assessing the environmental fate of certain organophosphate and organophosphorothionate esters may be estimated by use of linear free energy relationships (LFERs). LFERs for the second-order alkaline hydrolysis rate constants and the pK_a of the conjugate acid of the leaving groups were established for 0,0-dimethyl- and 0,0-diethyl-O-substituted phosphates and phosphorothionates. Also, the second-order alkaline hydrolysis rate constants of selected triaryl phosphates were correlated with the Hammett-sigma constants. Existing LFERs for diaryl phosphate ester anions along with monoaryl phosphate ester mono- and dianions were used to predict hydrolytic half-lives under reaction conditions that are characteristic of aquatic environments.

INTRODUCTION

The organophosphate triesters comprise a class of compounds widely used in agriculture as pesticides, in heavy industries as hydraulic fluid additives, and in petrochemical industries as plasticizers[1,2]. The agrochemical industry also manufactures organophosphorothionate triesters for use as pesticides[2]. Despite the extensive production and resultant widespread exposure of environmental compartments to various amounts of these compounds, surprisingly few quantitative data on their hydrolytic reactivity are reported in the open literature. This lack of information is particularly surprising because hydrolytic transformation is proposed to be an important pathway for the degradation of these compounds in aquatic ecosystems[3]. Because of the diversity of structures that result from different combinations of 0,0,0-alkyl and aryl substituents, however, one would anticipate a wide variation in hydrolytic reactivity under environmental reaction conditions in the water column.

To assess the fate and transport of these chemicals in aquatic environments, a systems approach that incorporates rate expressions describing the individual process is logical and useful. Such an approach requires values of the physical and chemical constants used in the rate expressions. Although measured values of these constants are not always available, estimates may be obtained by use of linear free energy relationships (LFERs). Such correlations are receiving increased attention in efforts to better describe environmental phenomena such as toxicity,[4] bioconcentration,[5] and sediment sorption.[6,7] By providing estimates of hydrolysis rate constants,[8] these LFERs or structure reactivity relationships are particularly applicable to the assessment of hydrolytic reactivity of organic compounds. Also, hydrolytic stability for classes of compounds can be readily evaluated.

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DISCUSSION

Two criteria are required to estimate rate constants by use of LFERs[9]: a readily available physical or chemical parameter to correlate with the rate constant and a data base of rate constants for compounds in the class of interest. Ideally, the rate constants for the data base are obtained under the same reaction conditions thus reducing the number of variables that can affect the measurements. The relationship, if one exists, is then described by a linear equation established through linear regression analysis. Finally, rate constants for other compounds of the same chemical class reacting by the same mechanism are calculated using the equation and the selected parameters of the compound.

Correlations

Two specific correlations are particularly suited to an environmental assessment of phosphate and phosphorothionate triester hydrolysis. The first is that of the first- or second-order hydrolysis rate constant (k) with the pK_a of the conjugate acid of the leaving group that results from hydrolysis (equation 1)[9].

$$\log k = m\, pK_a + C \qquad (1)$$

where m is the slope and C the intercept.

The second is a correlation between the first- or second-order hydrolysis rate constant (k) and the Hammett substituent constant (σ) given by equation 2

$$\log k = \rho\sigma + \log k_o \qquad (2)$$

where ρ is the slope and k_o the rate constant for the unsubstituted compound in the series[9].

The advantages of equation 1 for describing hydrolysis of phosphate and phosphorothionate esters are that alkyl, as well as aryl leaving groups, can be included in the correlation. Also, in the case of aryl groups, the correlation is not restricted to benzene derivatives as the leaving group. This equation allows the correlation of hydrolysis rate constants over a larger range of reactivity (pK_a 1 to 16). The disadvantage is that the pK_a's of the conjugate acid of the leaving groups are not always readily available. The advantage of equation 2 is that σ constants that have been determined for a large number of substituents are used. The disadvantage is that it is only applicable to phosphate and phosphorothionate esters for which the conjugate acid is that of a phenol or aryl moiety.

Kinetic expressions

Organophosphate and organophosphorothionate triesters, depending on the substituents, may undergo acid catalyzed hydrolysis, second-order alkaline hydrolysis, and neutral hydrolysis (sometimes referred to as solvolysis)[10-12] Generally, the acid catalyzed reaction for these esters is too slow to warrant any consideration under environmental reaction conditions. On the other hand, second-order alkaline hydrolysis and neutral hydrolysis reactions are more likely to occur and should be addressed.

The overall disappearance rate expression applicable to aquatic ecosystems is

$$-\frac{d[P]}{dt} = \left(k_{H_2O} + k_{OH}[OH]\right)[P] \qquad (3)$$

where [P], k_{H_2O}, and k_{OH} are the phosphate ester concentration, neutral first-order hydrolysis rate constant, and second-order alkaline hydrolysis rate constants, respectively[7].

Reaction pathway

The alkaline and neutral hydrolysis pathways may not give the same products depending on the structure of the ester groups (Figure 1)[12-15]. This is because hydroxide is about 10^8 times better as a nucleophile than water towards the phosphorous atom but only 10^4 times better as a nucleophile towards saturated carbon.[14] Three general cases are considered:

1. $R_1 = R_2 = R_3$ = aryl
   Neutral and alkaline hydrolysis products will be the same.

2. $R_1 = R_2 = R_3$ = alkyl
   Neutral and alkaline hydrolysis products will be the same.

3. $R_2 = R_3$ = alkyl and R_1 = aryl

   Neutral hydrolysis will result in loss of R_2 or R_3.
   Alkaline hydrolysis will result in loss of R_1.

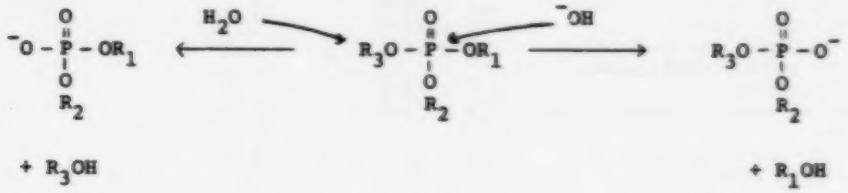

Figure 1. Reaction pathway for the neutral and alkaline hydrolysis of organophosphate triesters.

Hydrolysis rate constants

Table 1 contains the hydrolysis rate constants for the esters that were correlated in this study. Although no attempt was made to include the rate constants for all the phosphate and phosphorothionate esters reported in the literature, rate constants that were believed to be reliable, based on the experimental procedure, were utilized to provide a data base for the correlations.

O,O-Dialkyl-O-substituted phosphates

Figure 2 contains the plots of the log of the second-order alkaline hydrolysis rate constants versus the pK_a's of the conjugate acid of the leaving groups for a series of O,O-dimethyl and O,O-diethyl esters. The half-life values are also given, assuming pseudo-first-order reactions, for pH 8. This correlation includes both aryl and alkyl moieties as leaving groups. For the O,O-diethyl series, the slope of the line (m), which is a measure of the sensitivity of the reaction to structural change, is -0.28 ± 0.06 ($r^2 = 0.926$). This is similar to the O,O-diethyl series where m is -0.28 ± 0.04 ($r^2 = 0.974$).

Based on these correlations, it is apparent that the O,O,O-trialkyl phosphate esters will undergo alkaline hydrolysis very slowly at most environmental pH's. When the pK_a of the conjugate acid of the leaving group is about 10 (as it is for phenol, for example), the hydrolysis half-life is about a year. Thus, only when strongly electron withdrawing groups are present on the aromatic ring, providing leaving groups with pK's below 10, will alkaline hydrolysis readily occur at the alkaline pH's common to natural waters.

O,O-Dialkyl-O-substituted phosphorothionates

Correlations of the second-order alkaline hydrolysis rate constants with the pK_a's of the conjugate acid of the leaving groups are shown in Figure 3 for two different series of these compounds. For the O,O-diethyl substituted compounds, m is -0.21 ± 0.04 ($r^2 = 0.945$), which is close to the value of -0.25 ± 0.02 ($r^2 = 0.966$) for the O,O-dimethyl series.

Table 1. Second-order Alkaline Hydrolysis Rate Constants along with Sigma Constants and pK_a's of the Conjugate Acid of the Leaving Groups Used in the Correlations.

Triester	k, $M^{-1}sec^{-1}$, 27°	pK_a*	σ^+	Ref.
1) Diazoxon	7.6×10^{-2}	1.86**		3
2) Paraoxon	2.67×10^{-2}	7.15		16
3) Diethyl phenyl phosphate	1.0×10^{-3}++	10.00		19
4) Triethyl phosphate	1.75×10^{-5}	15.5		17
5) Methyl paraoxon	4.69×10^{-2}	7.15		16
6) Dimethyl phenyl phosphate	3.4×10^{-3}++	10.00		27
7) Trimethyl phosphate	2.0×10^{-4}	15.5		19
8) Diazion	5.2×10^{-3}	1.86**		3
9) Parathion	1.2×10^{-3}	7.14		20
10) Diethyl phenyl phosphorothionate	3.2×10^{-4}	10.00		18
11) Triethylphosphorothionate	6.4×10^{-6}	15.5		18
12) Methyl parathion	5.3×10^{-3}	7.15		12
13) Dimethyl-p-nitro-o-chlorophenyl phosphorothionate	1.8×10^{-2}	6.1		18
14) Fenitrothion	4.2×10^{-3}	7.2		28
15) Dimethyl phenyl phosphorothionate	2.2×10^{-3}++	10.00		27
16) Trimethylphosphorothionate	4.8×10^{-5}	15.5		18
17) Triphenyl phosphate	2.7×10^{-1}		0.0	18
18) Tri p-toluyl phosphate	2.5×10^{-1}		-0.207	18
19) Tri(p-nitrophenyl)phosphate	3.6×10^{2}++		2.13	19
20) Diphenyl (p-nitrophenyl)-phosphate	2.4++		0.71	21

*pK_a values are from Kortum et al. (26). +σ values are from Shorter (9).
**pK_a of 4-oxy-pyrimidin. ++Corrected for solvent effect.

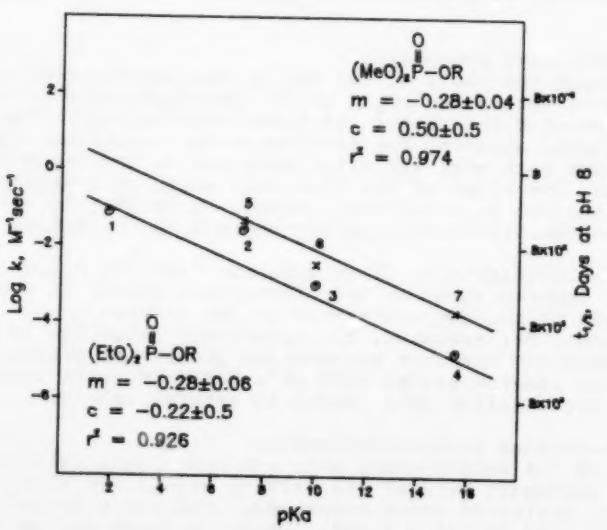

Figure 2. Linear free energy relationship for the alkaline hydrolysis of 0,0-dimethyl and 0,0-diethyl-O-alkyl and aryl phosphates in water at 27°.

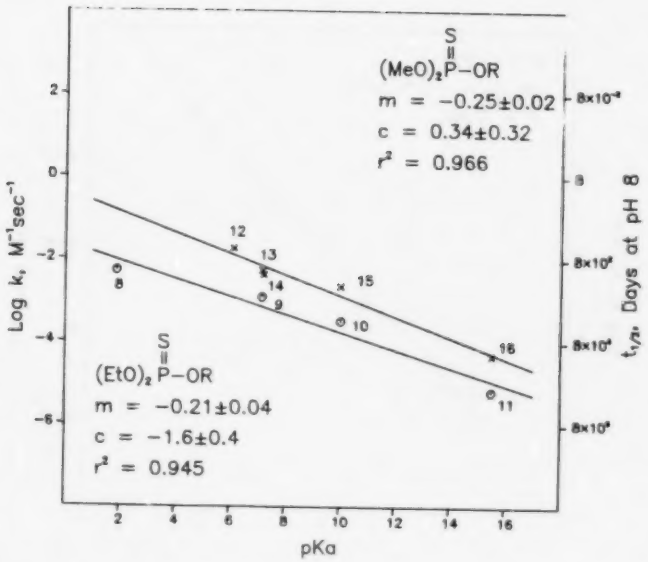

Figure 3. Linear free enrgy relationships for the alkaline hydrolysis of 0,0-dimethyl and 0,0-diethyl-O-alkyl and aryl phosphorothionate in water at 27°.

These correlations show that the phosphorothionates are less reactive than the corresponding phosphate esters. Again when the leaving group is an alkyl moiety, hydrolysis will be slow under most environmental conditions. Even when the leaving group is a substituted phenol with electron withdrawing groups, hydrolysis will be slow at pH's that occur in natural waters.

0,0,0-Triaryl phosphates

Limited hydrolysis data for some triaryl esters are presented in Figure 4. Correlation of the second-order-alkaline hydrolysis rate constants with the sum of the sigma substituent constants, $\Sigma\sigma$, gives a slope, ρ, of -0.47 ± 0.11 ($r^2 = 0.990$). An inspection of the calculated half-lives at pH 8 (Figure 4) assuming pseudo-first-order kinetics shows that hydrolysis half-lives are short at the alkaline pH's of many natural waters.

Neutral hydrolysis of aryl phosphate esters

It is more difficult to estimate neutral hydrolysis rate constants for environmentally important phosphate triesters because a significant data base is not always available to establish a correlation. One such study, however, suggests the use of this approach to the neutral hydrolysis reaction. The lack of complete data, however, does not preclude some insight into the hydrolytic behavior of certain classes of phosphate esters. Khan and Kirby[22] studied the neutral hydrolysis of four 2-aryl-oxy-2-oxo-1,3,2-dioxaphosphorinans and reported a correlation between the pK_a of the conjugate acid of the leaving groups and the first-order hydrolysis rate constant (Figure 5). For this series, calculated neutral hydrolysis half-lives are quite long, as shown by a half-life of about 10^4 days for phenol, a leaving group having a pK_a of 10.

Triaryl phosphate neutral hydrolysis rate constants can be evaluated even though an extensive data base is not available. For example, tri-(p-nitrophenyl)phosphate ($k = 1 \times 10^{-8}$ sec^{-1}, 25°) has a calculated half-life of

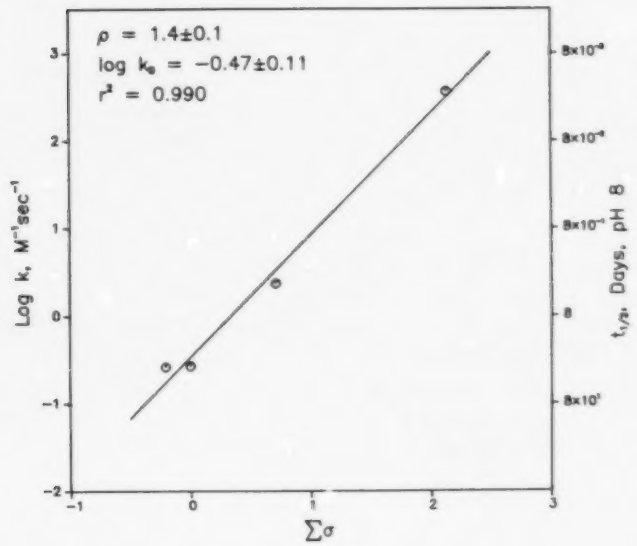

Figure 4. Linear free energy relationships for the alkaline hydrolysis of 0,0,0-triaryl phosphate ester in water at 30°.

about 800 days. If one assumes that a correlation exists between the triaryl phosphate hydrolysis rate constant and the pK_a of the conjugate acid of the leaving group and that the slope is similar to that of the phosphorinans (25°), then a linear equation is defined:

$$\log k = -0.95\ pK_a - 1.20 \qquad (4)$$

Based on this analysis, triphenyl phosphate would have an estimated hydrolysis half-life of about 10^3 years.

Neutral hydrolysis of phosphate diester anions and phosphate monoester anions

Phosphate triesters either directly through manufacturing wastes or indirectly through environmental transformation processes can give rise to phosphate mono- and diesters. It is desirable therefore to be able to assess their hydrolytic reactivity. Work by Kirby and co-workers[22-24] along with Bunton and co-workers[25] provides the necessary data base and correlations to estimate selected neutral hydrolysis rate constants. Figure 5 contains a LFER for the anions of five diaryl phosphates. At most environmental pH's, the diaryl esters will be dissociated and hydrolysis of the anion by hydroxide will not be important, but neutral hydrolysis of the anionic diester must be considered. Figure 5 shows that these esters are even less labile to hydrolysis than the triesters, and based on the calculated half-lives, neutral hydrolysis will be slow in aquatic systems.

LFERs for the neutral hydrolysis of mono- and dianions of phosphate monoesters and the pK_a of the conjugate acid of the leaving group are also given in Figure 5. Because the pK_a of the first dissociation step (pK_{a1}) is about 1.5 and the second step (pK_{a2}) is around 6 for most aryl esters, the mono- and dianions will be the dominant species at common environmental pH's. The observed rate constant can be calculated by

$$k_{obs} = k_m(F) + k_d(1-F) \qquad (5)$$

where F, the fraction of the monoanion, is approximated by $([H^+]/[H^+]+K_{a2})$ and k_m and k_d are the rate constants for mono- and dianions, respectively, obtained from Figure 5. Based on calculations of k_{obs} using equation 5 and these correlations, aryl and some alkyl monoesters are labile to neutral hydrolysis over the pH range of 5 to 7. At pH 6 for example, the neutral hydrolysis half-life for phenyl phosphate is estimated to be less than 80 days.

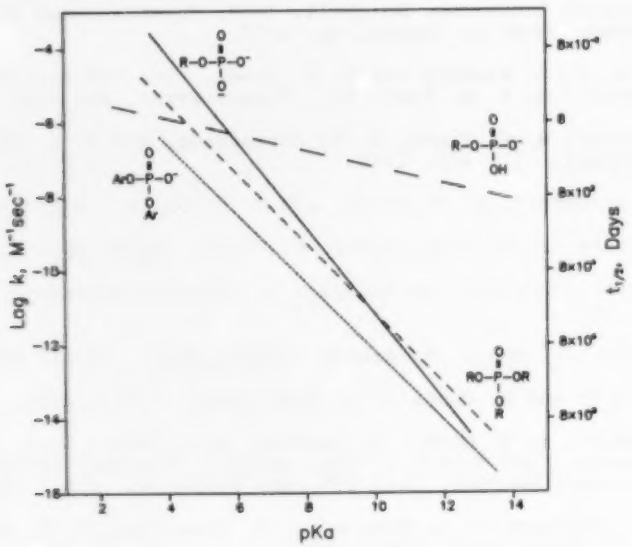

Figure 5. Linear free energy relationships for the neutral hydrolysis of phosphate tri-, di-, and mono-esters in water at 25°. The equations for the lines were recalculated for 25° using the data in references 16 and 22-25. The equations are: monoesters dianions, log k = -1.17 pK_a + 0.52; monoesters monoanions, log k = -0.22 pK_a - 5.01; triesters, log k = -0.95 pK_a - 1.67; diesters monoanions; -0.93 pK_a - 2.89

CONCLUSIONS

LFERs for the alkaline hydrolysis of 0,0-diethyl and 0,0-dimethyl-0-substituted phosphates and phosphorothionates indicate that in general alkaline hydrolysis half-lives will be long at alkaline pH's common to aquatic environments. In many cases where the LFER indicates the half-life is on the order of years, this estimate may well be satisfactory for fate assessment. In the case of 0,0-dimethyl-0-aryl substituted phosphates where half-lives can be on the order of a few months, an experimentally determined rate constant might be desirable. The triaryl phosphates are more susceptible to alkaline hydrolysis with half-lives on the order of a few hours at alkaline pH's of aquatic ecosystems. For these reactive esters, an estimate of the rate constant could be adequate for fate assessment. LFERs for the various phosphate anions indicate that the monoalkyl and aryl phosphate monoanions are generally the most susceptible to neutral hydrolysis.

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